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Physical properties of Ce_2CoSn_2

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Abstract

A complete physical characterisation, through specific heat, electrical resistivity and magnetization measurements was performed, in a wide temperature range, on the new phase Ce_2CoSn_2, which crystallizes in a very large fcc cell with a structure type similar to the $Tb_{117}Fe_{52}Ge_{112}$ one. From the real part of the AC susceptibility data a broad maximum can be observed at 7 K with an inflexion point, in agreement with the maximum observed in the imaginary part of the AC susceptibility, at a lower temperature (around 6 K). We hypothesize that the lower maximum can be attributed to an antiferromagnetic transition while the upper one could be related to the onset of a Kondo regime. The antiferromagnetic order is confirmed by magnetization measurements performed at 2 K in magnetic fields up to 9 Tesla: a metamagnetic transition could be observed around 0.4 Tesla. In the paramagnetic range the inverse of susceptibility follows a modified Curie–Weiss law, with an effective paramagnetic moment $\mu = 2.89\ \mu_B$ and a paramagnetic Curie temperature slightly positive. The heat capacity results suggest that this phase might be a heavy fermion system, with an electronic specific heat coefficient $\gamma = 1.3\ J/K^2$ mol. The electrical resistivity measurements exhibit a pronounced minimum at about 13 K and below this temperature a logarithmic Kondo-like behaviour is observed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cerium intermetallics; Rare earth cobalt stannides; Physical properties; Heavy fermion behaviour

1. Introduction

Ternary cerium compounds have been carefully investigated in the past, since they have a wide variety of anomalous physical properties: intermediate valence, Kondo effect and coexistence of heavy fermion behaviour with interesting magnetic orderings at low temperatures are often observed in this phases [1–8].

Most of these peculiar properties can be ascribed to the appearance of a resonant peak in the density of states (DOS) at the Fermi level (E_F) below a characteristic temperature, and described in the framework of the Abrikosov–Suhl's model [9]. This effect, giving rise to an anomalous increase of the DOS at E_F, produces electronic anomalies experimentally observed as: a high coefficient of the electronic heat capacity, logarithmic Kondo-like behaviour of the electrical resistivity, enhanced value of the Pauli paramagnetism.

Searching in the ternary systems R–Co–Sn (R=rare earth), for materials with technologically stimulating magnetic properties, the new phases $R_3Co_8Sn_4$ (R=Pr to Lu) [10] and $R_4Co_2Sn_5$ (R=La, Ce) [11] were found to be stable at room temperature and were investigated by our group. Moreover, while studying the latters, a new family of ternary rare-earths intermetallic compounds was identified, whose stoichiometry was found by microprobe analyses to be R_2CoSn_2; the existence of this composition has been ascertained for at least all the light R from La to Sm, but preliminary results would indicate its formation also for the heavy R. At present a complete crystallographic investigation on light R_2CoSn_2 (R=La, Pr, Nd, Sm) single crystals is in progress in our laboratory in order to define exactly the stoichiometry of the phase.

The purpose of this paper is to present a rather complete physical characterisation of the Ce_2CoSn_2 intermetallic compound, through electrical resistivity, magnetization and heat capacity measurements.

2. Experimental

The metals used were high purity commercial products: 99.9 wt.% purity for both cerium and cobalt and 99.999 wt.% for tin. Samples were prepared by melting stoichiometric amounts of the elements in form of turnings and pressed into a pellet (cerium was worked up in argon atmosphere). A larger sample for the calorimetric charac-

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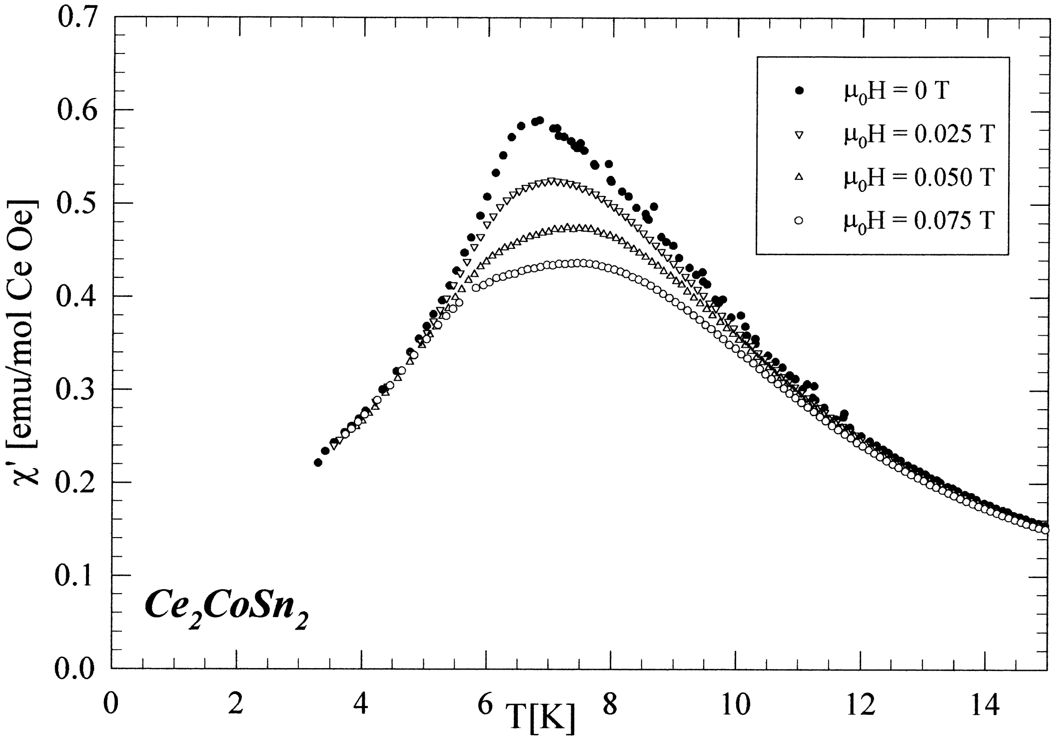

Fig. 1. Real part χ' of the AC magnetic susceptibility between 4 and 15 K as a function of the applied magnetic field.

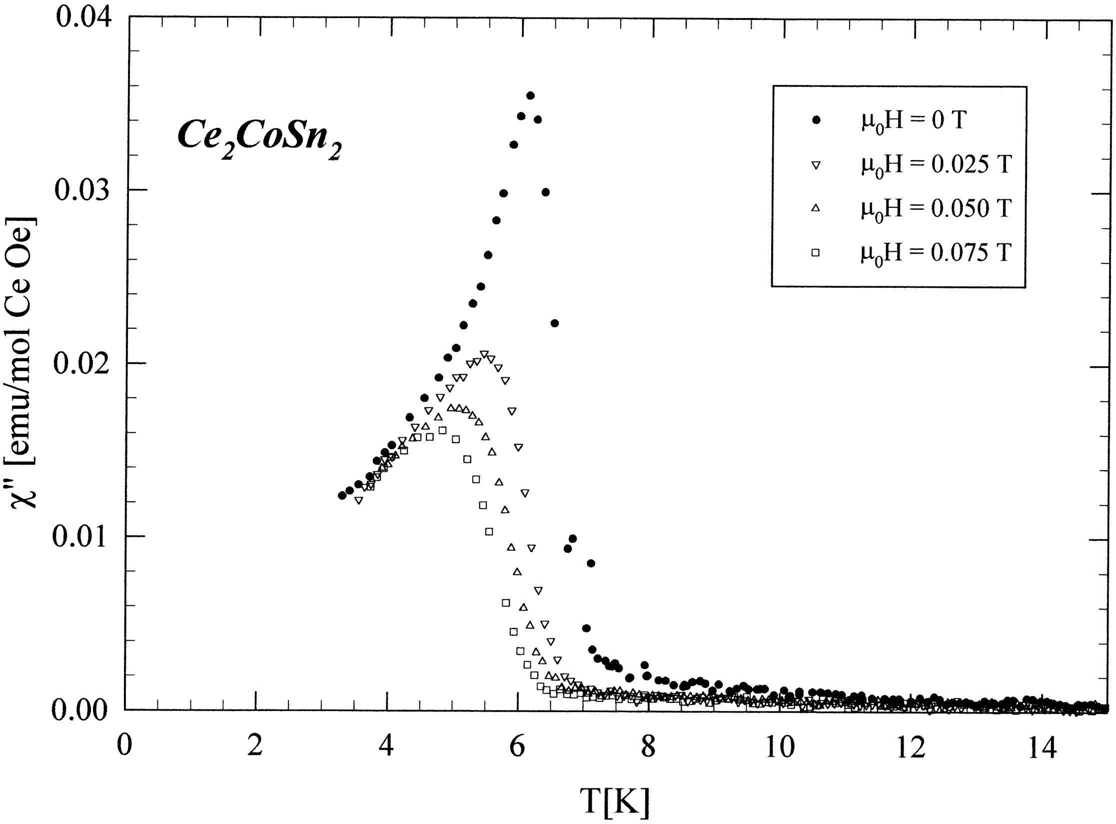

Fig. 2. Imaginary part χ'' of the AC magnetic susceptibility between 4 and 15 K as a function of the applied magnetic field.

terisation has been therefore prepared by slow induction melting in a high-frequency furnace on a water-cooled copper hearth under pure argon atmosphere; despite the method adopted, to avoid the breaking of the button while remelting to ensure complete homogenisation or on cooling, a following melting under vacuum has been essential. The alloys prepared in this way did not undergo weight losses even if vacuum melted. Annealing is necessary because, as suggested by differential thermal analysis data, these R_2CoSn_2 intermetallics have a peritectic formation: thus Ce_2CoSn_2 has been annealed at 800°C for 2 months.

All the samples were analyzed using standard metallographic techniques, electron microscopy and microprobe analysis: micrographic examination showed that the compound was a single phase constituted by large polygonal grains with, all around its border, very little of grain separation (1% at most). X-ray powders analysis was carried out by means of a Guinier camera, using CuKα radiation and silicon as internal standard (a=5.4308 Å). Diffraction patterns were calculated using the Lazy Pulverix program [12].

Electrical resistivity data were collected, with a standard four-point DC method, in the 4.2–300 K temperature range on a specimen of approximate dimensions: 1×1×5 mm^3.

Magnetization, heat capacity (adiabatic method) and AC susceptibility measurements were performed by an Oxford $Maglab^{2000}$ platform system, operating in the 2–300 K temperature range and in applied magnetic fields up to 9 Tesla (T). The heat capacity data were collected on a sample of 1.3 g. The temperature sensor used for the calorimetric measurements was a calibrated Cernox-type thermometer from Lake Shore Cryotronics Inc.

3. Results and discussion

X-ray powder patterns showed a very large face-centred cubic cell, with a lattice constant of the same order of magnitude of that reported in literature for the fcc structure of the $Tb_{117}Fe_{52}Ge_{112}$-type [13] (space group F m $\bar{3}$ m) with a presumable high number of non-equivalent Ce sites. X-ray intensity calculations were carried out to compare with the experimental ones but only resemblance and no agreement was found. The lattice constant obtained for Ce_2CoSn_2 is a=31.97(4) Å. Single crystal X-ray diffraction measurements are in progress in order to determine the crystal structure.

The AC susceptibility measurements, with an AC field of 1 Oe (ω=977 Hz) were performed at 0, 0.025, 0.05 and 0.075 T applied fields and the results of the real (χ') and

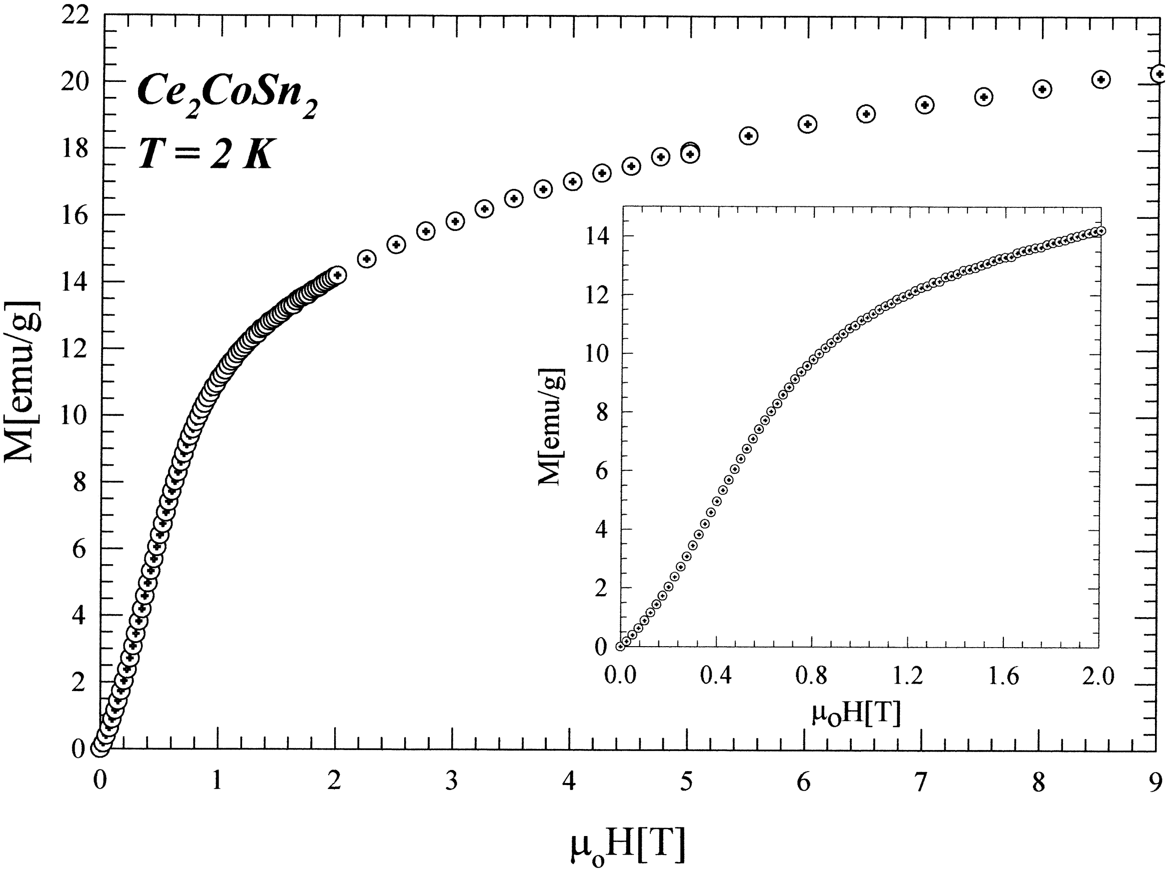

Fig. 3. Magnetic field dependence of the magnetization of Ce_2CoSn_2 at T=2 K.

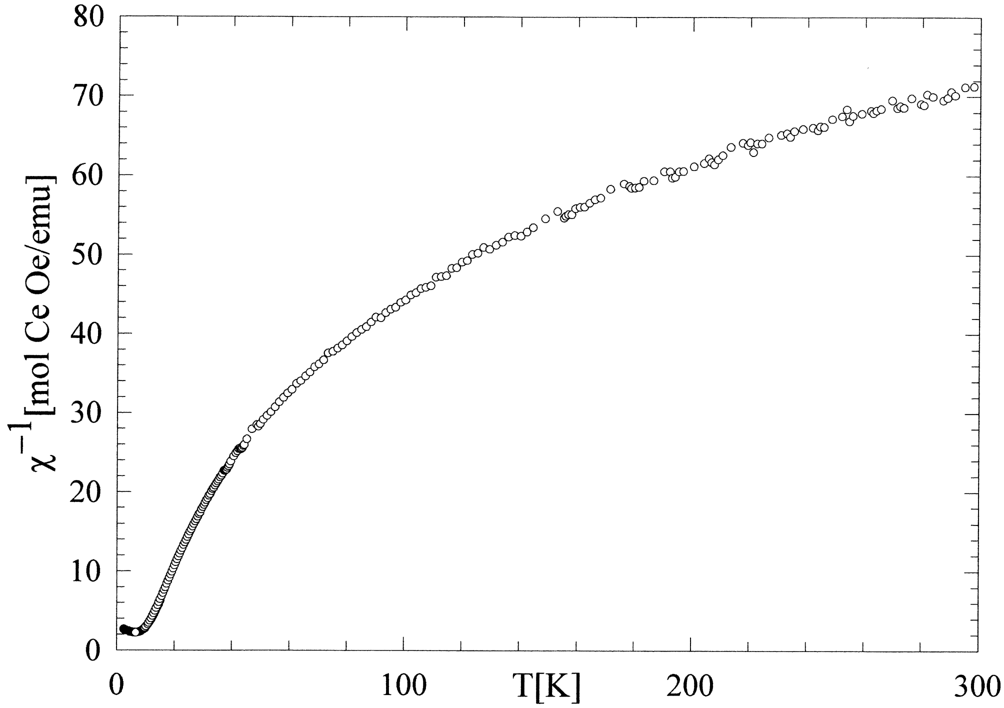

Fig. 4. Inverse of the magnetic susceptibility of Ce_2CoSn_2 between 5 and 300 K.

imaginary (χ'') part of the susceptibility are shown in Figs. 1 and 2, respectively. The real susceptibility at $\mu_0H=0$ T shows a broad maximum at 7 K followed by an inflexion point around 6 K. Under the influence of the DC applied magnetic field the value of the maximum decreases and shifts towards higher temperatures. A different behaviour can be observed from χ'': at zero magnetic field we observe a quite sharp maximum centered at 6.1 K, which corresponds to the inflexion point detected from χ'. The magnetic field strongly suppresses the value of the maximum and shifts it toward lower temperatures, i.e. a typical trend of an antiferromagnetic ordering. Moreover above 7 K the values of χ'' are almost constant and quite independent from temperature and applied magnetic field.

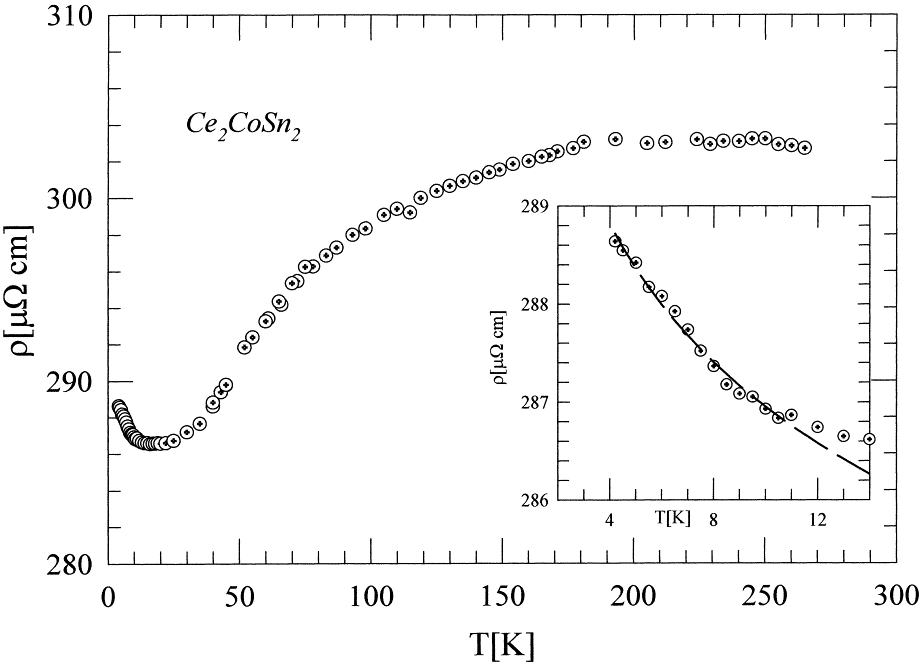

Fig. 5. Electrical resistivity of Ce_2CoSn_2 in the 4 – 300 K temperature range. In the inset the dashed line marks the logarithmic behaviour.

Following Fourgeot et al. [8], we hypothesize that also in Ce_2CoSn_2 two characteristic temperatures can be detected: the first, which corresponds to the broad maximum of χ' can be ascribed to the temperature where the effect arising from spin fluctuations in the Kondo regime is maximum, while the second one, i.e. the sharp maximum of the imaginary susceptibility, is related the onset of the antiferromagnetic order. The hypothesis of antiferromagnetic interactions below 6 K are confirmed by the field dependence of the magnetization performed at 2 K, the lowest temperature achievable, and reported in Fig. 3. The magnetization increases sharply up to 2 T, then continuously up to 9 T without saturation. The maximum value detected at 9 T corresponds to 1.06 μ_B/Ce atom, which is approximately half of the theoretical value in the ordered state (μ_{gJ}=2.14 μ_B). Low values of the Ce magnetic moment in the ordered state have been already observed in other Ce compounds [4–6]. From the inset of the same figure, where the low field (0–2 T) measurements are reported, we observe the broad metamagnetic transition, which occurs around 0.3 T. In Fig. 4 the inverse of the magnetic susceptibility is reported. In the paramagnetic region, the Curie–Weiss law is not followed but the experimental data could be well fitted, in the 10–300 K temperature range, by a modified Curie–Weiss law:

$$\chi = \chi_0 + \frac{C}{T - \theta}$$

where χ_0 represents the temperature-independent part of magnetic susceptibility and includes the diamagnetic core contribution, the Pauli paramagnetism and the Van Vleck correction, and θ is the asymptotic paramagnetic Curie temperature. This equation works well for materials like Kondo systems or displaying valence fluctuation behaviour, such as Ce_2Ni_2Cd [1], CeIrGe [2], $CeRuGe_3$ [6]. A least squares fit yields an effective magnetic moment μ_{eff}=2.89 μ_B, a paramagnetic Curie temperature slightly positive θ=7.2 K and χ_0=1.1·10^{-2} emu/mol Ce. The value of the observed moment, although slightly higher than that calculated from the Russell–Saunders coupling, suggests that the effective cerium valence is 3^+ in this compound. The positive Curie temperature implies the coexistence of ferro- and antiferro-magnetic interactions in agreement with the metamagnetic behaviour observed from magnetization data.

The temperature dependence of the electrical resistivity for the Ce_2CoSn_2 intermetallic compounds from 4 to 270 K is shown in Fig. 5. In the temperature range between 200 and 270 K the shape is rather flat with a slight increase to temperature decreasing. Below 200 K the resistivity decreases more rapidly down to a very large minimum around 15 K and finally, at temperatures just below this minimum, the resistivity values increase. As reported by a dashed line in the inset of the same figure, in the 4–12 K range the experimental data, under the hypothesis that the phononic contribution could be neglected in this temperature range, were well fitted by the following equation:

$$\rho(T) = A - B \ln T$$

characteristic of a Kondo-like behaviour, as observed in other heavy fermion systems [14,15]: we found **A**=291.6 μΩ cm and **B**=2.04 μΩ cm.

Low temperature heat capacity measurements are shown in Fig. 6(a). No evidence of the antiferromagnetic order can be detected from the experimental heat capacity data. In Fig. 6(b) the calorimetric measurements are reported as C_p/T vs. T^2. A deep minimum can be observed at 13 K: below this the C_p/T values increase sharply with decreasing temperature down to the lowest temperature explored (3 K). Again the hypothesis of heavy fermion behaviour with anomalous high values of the effective mass of the conduction electrons could explain this trend: i.e. below 13 K the electronic coefficient γ of the heat capacity increases anomalously. If this electronic contribution is quite high, in this case it might hide the magnetic specific heat, as in this compound. The extrapolation of the low (3–9 K) C_p/T data allow to obtain the γ value: γ=1.3 J/K^2 mol, which can be compared with other abnormally high values

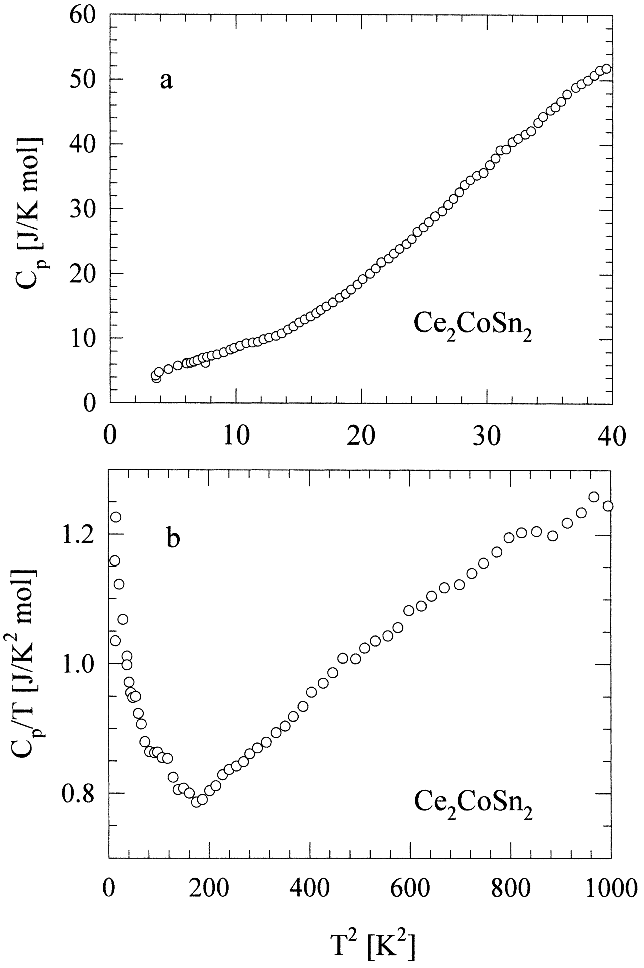

Fig. 6. (a) Specific heat of Ce_2CoSn_2 between 3 and 40 K and (b) C_p/T vs. T^2.

observed in well known heavy fermion systems as $CeCu_6$, $CeAl_3$ [16] and UBe_{13} [17].

In conclusion, from AC susceptibility, electrical resistivity and low temperature heat capacity measurements we have found that in the ternary compound Ce_2CoSn_2 an antiferromagnetic state exists in the Kondo regime: the system undergoes in the Kondo state below 13 K and orders antiferromagnetically at 6 K. As the physical properties of this compound may be strongly influenced by the crystal structure, works are in progress in order to determine and define the exact stoichiometry of this phase.

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